J. FAN and **S. ANANTHANARAYAN,** Advisian, a Worley Company; and **A. HODGKINSON,** Advisian, a Worley Company, Atlanta, Georgia

Demineralized water system design: Considerations for the petrochemical industry—Part 1

Site utility leads, engineers and other professionals in the hydrocarbon/chemical processing industries (HPI/CPI) are facing a perfect storm of increasing demineralized water demand, end of life of existing demineralized water plant equipment, changing source water quality, corporate directives to diversify water sources, and pressure from regulators and community stakeholders to minimize the volume of waste generated from water treatment. The last decade has seen large-scale investment in ethane crackers, and a second wave of crackers are being designed and engineered that will begin service in the next few years. These investments have resulted in a keen focus on raw water treatment and demineralization for steam production, which, along with ethane, is a basic input to the cracking process. Many refineries, especially those along the U.S. Gulf Coast, have also seen increased demineralized water demands as they upgrade their operations to produce higher-value products. The main steam uses in refineries include steam cracking, stripping, steam distillation and vacuum distillation. Steam is also used for process heating, pumping and electric power generation.

Over the last 10 yr to 15 yr, these developments have coincided with increased water stress from both droughts and floods in various watersheds tapped by HPI/CPI for their source water. Key design considerations and approaches utilized in demineralized water treatment system design for HPI/CPI are presented in this article. Alternatives for demineralization systems are compared and analyzed, and key decision-making criteria are discussed to introduce utility engineers and professionals to the thought process behind demineralized system design. The choice of demineralized water treatment technology boils down to several factors, including the type of raw water, temperature and associated chemistry, nature of demineralized water demand and quality of steam required (mainly the pressure). Constraints related to the footprint (especially in brownfield developments) and any wastewater volume limitations at the site should also be considered in the design process.

Source water.

The following are types of source water that can be used in processing plants.

Surface water. Surface water sources for demineralized water treatment include rivers, lakes and oceans. Overall, 72% of all water used by refineries in the U.S. is drawn from rivers and lakes.[1] Surface water is most often pumped directly from a water body or drawn through a canal by a quasi-state body, which then supplies the water to several industrial customers. However, the total volume allocated to users might be regulated by state or local authorities to ensure that supply is available for all users. Seawater is also used for once-through cooling in some coastal refineries. The use of seawater is limited to coastal refineries and chemical facilities due to high conveyance cost and associated corrosion-resistance material requirements. In addition, high ionic strength, compositional variability in estuarine locations, high suspended solids and macrofouling organisms all contribute to high maintenance cost and operational complexity in seawater systems.

Groundwater. It has been reported that 10% of the water used by refineries is drawn from groundwater.[2] Groundwater can be very hard, with high mineral content, making it more expensive than lake water to treat into demineralized water. Some brackish groundwater is also available as a water source, but its high cost of treatment limits its use by most refineries. Furthermore, there are concerns related to the settlement of ground due to long-term groundwater extraction. Groundwater also typically has higher concentrations of reduced ions—such as iron and manganese—which, when brought to the surface, will oxidize and require specialized pretreatment prior to handling in a demineralized system. Combined, these factors mean that groundwater rarely provides a significant portion of the demineralized water supply at most industrial facilities—although there are some exceptions in the absence of alternate water sources.

Municipal wastewater reuse. Municipal wastewater generally consists of grey water and black water. Grey water includes water from bathing, hand washing and clothes washing, while black water includes water from kitchens, sinks and toilets. The combination of grey water, black water and storm water is treated in a municipal treatment plant and the effluent could be used in a refinery for boiler feedwater with further polishing, particularly for trace organics. The cost of conveyance from municipal wastewater treatment plants (WWTPs) into the refinery, along with extensive pretreatment to remove soluble organic carbon, should be taken into consideration and will result in increased treatment complexity and higher capital and operating costs than in instances when a typical city water supply is used. A more common strategy is to reuse treated municipal wastewater for cooling, which, in turn, frees up surface water for use as feed for demineralized water treatment.

Industrial wastewater reuse. Wastewater generated from oil refinery and petrochemical plants could potentially be reused after further treatment, as cooling water offers the prospect of freeing up higher-quality raw water for demineralized water usage. Cooling system blowdown water is also a potential candidate for demineralized system source water, after further treatment. However, in contemplating cooling water for use as demineralized supply, the water chemistry and process design must be thoroughly reviewed, with special consideration given to the capability of the demineralized plant to handle condenser leak events in the cooling system. The benefits of reusing refinery wastewater include consistent water quantity and quality; reduced demand on other water sources; and reduced discharge to water bodies. Total dissolved solids (TDS) concentration is the primary concern of industrial wastewater reuse. A TDS concentration of 1,000 mg/l or less is generally considered acceptable for reuse as cooling water, fire water and wash water. Typically, reusing any type of wastewater, including from industry, requires evaluation on a site-specific basis regarding wastewater availability, reliability, quality, energy consumption and process design.

Reusing all industrial wastewater with no liquid waste stream discharged into the environment is termed *zero liquid discharge* (ZLD). This water reuse concept has the potential to produce a portion of its recovered water as a high-quality distillate, which is very suitable for supplementing demineralized water production. It should be noted that ZLD usually entails a high treatment energy requirement, high capital cost (due to the need for exotic metallurgy) and high operational complexity. A decision to pursue a ZLD outcome is typically driven by either severe water scarcity and/or regulations and is rarely considered as part of site demineralized water strategy.

Water quality characterization. It is critical that appropriate water quality characterization studies are undertaken at the outset of any demineralized plant design project. For a relatively small sum of money (low thousands of dollars vs. hundreds of millions of dollars required for the demineralized plant construction and the billions of dollars for the overall facility), a good water quality data set can be collected to characterize and select source water and decide treatment process configuration. Often, data is not collected or inadequately detailed (e.g., some parameters are not collected, or no data is collected during times when the river is in flood or at minimum flow). To prepare a robust system design, data covering all typical quality and flow scenarios giving a complete picture of the anticipated water quality in the watershed is required. Understanding trends in suspended and colloidal solids, including colloidal silica, can be very valuable in the design of the treatment system. Assessing the potential for algal blooms and any anecdotal data related to past bloom events (e.g., duration and frequency) is also helpful in designing an effective pretreatment process. At a minimum, seasonal data over a period of 5 yr–10 yr is typically used as a starting point for a water chemistry basis of design. If available, longer periods of data—from site records or publicly available databases—can also be helpful to understand longer-term trends.

Pre-treatment. Prior to demineralized water treatment, most raw water sources must first undergo pretreatment to remove suspended solids and reduce scale forming hardness and/or compounds that have a propensity to generate corrosion. Depending on the source of raw water, water chemistry varies significantly. Relative ranges for key parameters are shown in **TABLE 1.** Main contaminants of concern for boiler feedwater include:

- **Suspended solids.** Suspended solids will settle out on equipment surfaces and cause deposition.
- **Total hardness.** In most waters, nearly all hardness is due to calcium and magnesium. Hardness can cause scale in heat exchangers, pipe and vessel surfaces, resulting in unnecessary downtime and reduced process performance (e.g., in heat exchangers).
- **Silica.** Hard scales resulting from silica are called silica-based deposits. These result from either amorphous silica and/or magnesium silicate. Silica entering a boiler can also be carried with the saturated steam as silicic acid, which can cause precipitates on metal surfaces. Hence, silica is considered one of the most critical parameters in any demineralized water treatment system and it is essential to closely monitor and control silica in the demineralized water makeup supply and, in turn, the demineralized water.
- **Iron.** Soluble and insoluble iron will combine with phosphates and hydroxides to form scale and cause corrosion and overheating problems.
- **Dissolved solids.** High ranges of dissolved solids can cause process interference and foaming in the boiler.
- **Total organic carbon.** Under high temperature and pressure, organic compounds can break down and form carbonic acid in the steam and condensate. This results in an increase in the conductivity of the steam and reduced pH in the condensate, increasing the propensity for corrosion around the steam system.
- **Sodium.** Sodium can build up on critical components as steam condenses and causes embrittlement, leaks and cracks.

TABLE 1. Typical ranges of main contaminants from different source water[3,4,5,6]

	Suspended solids, mg/l	Total hardness as $CaCO_3$, mg/l	Silica, mg/l	Iron, mg/l	Dissolved solids, mg/l
Surface water, river/lake	60–2,000	10–180	5–30	0.5–1	100–2,000
Surface water, seawater	< 500	< 6,000	> 10	1–3	> 35,000
Groundwater	10–50	< 1,000	1–30	< 20	100–30,000
Municipal WWTP effluent	< 30	< 200	5–20	< 0.5	600–1,000
Industrial WWTP effluent			Site-specific data		

In demineralized treatment processes, it is critical that adequate pretreatment is used to remove colloidal materials and suspended solids. Otherwise, it can lead to the failure of the demineralized treatment system. The degree and complexity of the pretreatment equipment are determined by the raw water quality. In a small flow facility, a low level of suspended solids (< 30 mg/l) might be managed with just cartridge filtration. However, it is more common in the case of surface water for pretreatment to include disinfection, solids clarification and filtration. Two common pretreatment systems for suspended solids removal are media filtration and membrane filtration. The following will introduce these systems, along with their advantages and limitations.

Media filtration captures pollutants through physical filtration and adsorption. Typical media-based filtration systems are composed of sand, anthracite and other media. Media filtration can be utilized in either a fixed-bed or moving-bed configuration (**FIG. 1**). After a period in service (typically once per day or when differential pressure setpoint is triggered), fixed beds of sand and anthracite and/or other media combinations (housed in either pressure vessels or in concrete basins) are taken offline for backwashing (cleaning) to remove accumulated solids. This requires additional infrastructure (backwash tanks, associated pumps, sludge treatment, solids handling, etc.) and footprint. In a moving-bed (or continuous backwash sand filtration) configuration, the media is continuously backwashed and a separate backwash tank is not required. The backwash wastewater from both continuous backwash filtration and fixed-bed filtration are handled in similar fashion before disposal.

Sometimes, media filters are used to treat soluble components in the water, usually following the primary particle filtration step. The most commonly used media to remove soluble components include activated carbon (for organics) and zeolite (for removing hardness). A comparison of three types of media commonly used in media filtration is shown in **TABLE 2.**

Membrane-based filtration, using ultrafiltration (UF) membranes that have a pore size of around 0.05 µm, is another way to remove suspended solids. The thin, permeable, hollow-fiber membrane layer physically excludes particles in the water, allowing only soluble components (and the water itself) to pass through into the ultrafiltrate. Two main formats of membrane filtration systems exist: pressure and vacuum-driven. Pressure-driven membrane systems use membrane elements installed in pressure vessels, and the membrane separation process is driven at 20 kPa–250 kPa (3 psi–36 psi). Vacuum-driven systems immerse the membrane modules in a tank, and the filtrate is drawn through the membranes via suction. A comparison of media filtration and UF is provided in **TABLE 3.**

The selection and performance of pretreatment technologies largely depends on feedwater quality. UF usually shows better removal efficiency for total organic carbon (TOC) and turbidity as compared with media filters for river water.[7] UF is

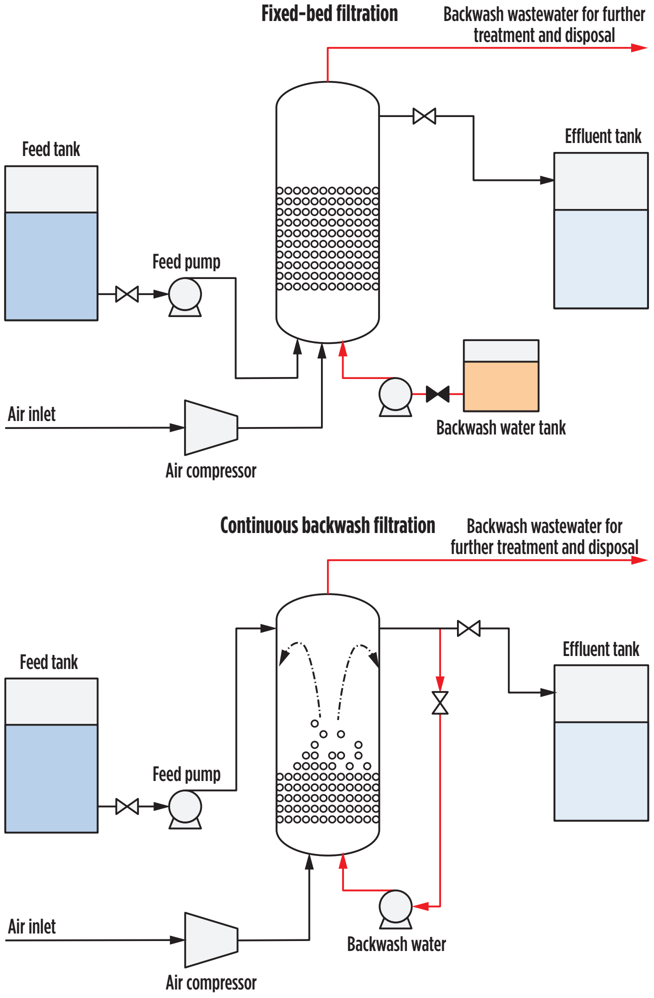


FIG. 1. Comparison between fixed-bed filtration and continuous backwash filtration.

TABLE 2. Common media used for filtration

Filtration media	Advantages	Limitations
Sand and other mixed-media formats	• Removal of suspended solids to less than 5 mg/l • Simple cleaning and inexpensive backwashing systems	• Water temperature should be less than 65°C (120°F) to avoid pickup of silica • Does not remove dissolved solids
Activated carbon	• Removal of organics and chlorine residual to protect downstream unit operations, such as ion exchange and/or membranes • Can accommodate influent fluctuation in the concentration of chlorine or organics	• High cost of bed replacement • Can suffer attrition loss during backwashing
Zeolite	• Removal of hardness, iron and manganese • Not as commonly used as carbon and sand	• Stringent operating conditions: o pH: 6.6–8.8 o Maximum water temperature: 38°C (100°F)

also less susceptible to particle breakthrough and offers a more reliable barrier than media filtration. However, UF is more sensitive to algae blooms, high natural organic loading, reactive species such as manganese, certain types of colloidal contaminants and water temperature variation. Increased biofouling has been observed on UF, compared to media filters for seawater pretreatment, in some instances.[8] The selection and deployment of the most effective filtration solution should be based on site-specific water quality parameters. Other factors, such as footprint, construction cost and lifecycle costs, should also be considered in the final selection. If the filtered water is used as cooling tower makeup, the value of performance benefits from better-quality water (e.g., increased cycling of cooling towers and reduction in fouling of heat exchanger surfaces) should also be considered in the selection of filtration technology.

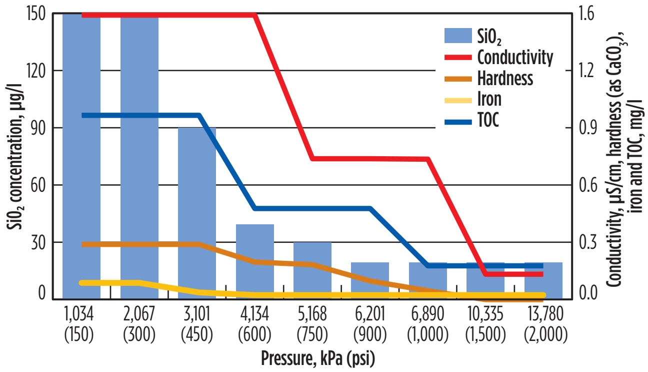


FIG. 2. Boiler feedwater quality requirements at various pressures. The actual target silicon dioxide (SiO_2) values in the demineralized water are set based on the site-specific considerations, including boiler cycles and types of metallurgy involved. Usually, the concentration will be in the range of 10 µg/l–20 µg/l for greater than 6,000 kPa (approximately 900-psi) steam.

After pretreatment, the feedwater—free of suspended solids—passes through the demineralized process to remove undesirable ions. These include heavy metals and, in most refineries, the entire dissolved solids content of the water. The target quality of demineralized water treatment depends on the pressure at which the boiler is operated. The general principle is that the higher the pressure, the higher the quality of water required. A low-pressure boiler can usually tolerate some feedwater hardness, while almost all impurities must be removed from water used for high-pressure boilers. Boiler feedwater quality requirements issued by the American Society of Mechanical Engineers (ASME) are shown in **FIG. 2.**

To ensure the purity of boiler feedwater, key parameters, such as TDS and silica, must be monitored. Conductivity is one of the most commonly used methods to obtain a rapid and reasonably accurate measurement of water/steam purity. However, some gases (especially carbon dioxide) can ionize in water solution and interfere with measurement of dissolved solids by increasing conductivity. The measurement of silica can use a colorimetric technique, while the reliability of this method is low under high temperature/pressure (form of silica can change from non-reactive colloidal form into reactive ionic form). Online measurement of sodium using specialized glass electrodes can provide a very sensitive indication of contaminants in water and/or steam condensates. Sodium measurement can give reliable measurements down to a concentration of 0.1 µg/l, which is well below the purity at which electrical conductivity can be measured reliably. However, sodium electrodes can be prone to drift and must be regularly calibrated. Each of these three methods can provide an indication of boiler feedwater purity, and the combination of any two generally provides reliable confirmation of boiler feedwater purity.

The common demineralizing technologies include ion exchange, reverse osmosis and electro-deionization. Frequently, a

TABLE 3. Selection guidance for media vs. membrane filtration

Criteria	Media filtration	Membrane filtration (UF)	Notes
Filtered water quality	–	+	Membrane filtration has a wider spectrum of particle removal capability than media filtration, as it represents a direct barrier to entry of contaminants. It generates higher-quality water (non-detect TSS and turbidity) on a consistent basis. It can remove colloidal silica.
Source water quality variation	–	+	Membrane filtration is better able to handle water quality variations, especially when combined with pre-clarification to keep gross solid loadings low.
Source water temperature	+	–	Throughput of membrane filtration is reduced at low temperatures.
Waste stream generation	+	–	Media filter backwash is 5%–7% of total feedwater, while membrane filtration backwash can be around 10%. Membranes may require additional cleanings and associated handling of cleaning waste.
Energy cost	+	–	Media filtration energy requirement is less than 0.05 kWh/m^3 and membrane filtration is 0.2 kWh/m^3–0.4 kWh/m^3.
Media replacement cost	+	+	Depending on how well either system is managed—can be comparable.
Capital cost	–	+	For large flowrates, UF may have a lower capital expenditure than media filtration. UF also tends to have lower installation costs, as UF is skid-mounted equipment that can be installed at a site quickly.
Footprint	–	+	UF has a lower footprint (typically 20%–30%) for the same flowrate.
Expandability	–	+	Modular design can permit easier staged expansion.

Note: (-) represents the less preferred option, while (+) stands for the preferred option[7] combination of these technologies is used to achieve the target water quality specification. Thermal methods to demineralize water, once quite common, especially in the Middle East, are now usually only considered in instances where a low-cost source of thermal energy is available.

Part 2. Part 2 of this article, to be published in the April issue, will discuss the common technologies and approaches considered for water demineralization and introduce the reader to demineralized water treatment design variables that must be considered for an effective design. HP

ACKNOWLEDGEMENTS

The authors would like to thank Karen Leber for her contribution to this article.

LITERATURE CITED

[1] Blieszner, J., R. Henderson and L. Weaver, "Potential vulnerability of U.S. petroleum refineries to increasing water temperature and/or reduced water availability," U.S. Department of Energy, January 2016.

[2] Sun, P., et. al, "Estimation of U.S. refinery water consumption and allocation to refinery products," *Fuel,* June 2018.

[3] Nasrabadi, T., et. al., "Bulk metal concentrations versus total suspended solids in rivers: Time-invariant and catchment-specific relationships," *PloS one,* January 2018.

[4] "Iron and water: reaction mechanisms, environmental impact and health effects," Lenntech, https://www.lenntech.com/periodic/water/iron/iron-and-water.htm

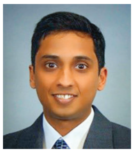
[5] "Hardness in groundwater," Water Stewardship Information Series, February 2007, https://www.rdn.bc.ca/cms/wpattachments/wpID2284atID3802.pdf

[6] Houston Public Works water quality report, 2017, https://www.publicworks.houstontx.gov/sites/default/files/images/utilities/wq2016.pdf

[7] Abbasi-Garravand, E., et. al., "Using ultrafiltration and sand filters as two pretreatment methods for improvement of the osmotic power (salinity gradient energy) generation process," 4th Climate Change Technology Conference, Montreal, Canada, 2015.

[8] Badruzzaman, M., et. al., "Selection of pretreatment technologies for seawater reverse osmosis plants: A review," *Desalination,* January 2019.

JINGJING FAN is a Wastewater Process Engineer at Advisian, a Worley Company. She has experience in water and wastewater treatment design for the petrochemical and refining industries. Dr. Fan holds a PhD in environmental engineering from the University of Houston.



SRIRAM ANANTHANARAYAN is a Lead Process Engineer/Project Manager with Advisian, a Worley Company. Mr. Ananthanarayan has more than 15 yr of experience in the process design, engineering and evaluation of water and wastewater treatment systems. He has led and developed designs to support projects in the oil and gas, chemicals, power and mining industries. He earned a BS degree in chemical engineering from the University of Calicut and an MS degree in civil engineering from Colorado State University.

ANDREW HODGKINSON is the Global Technical Leader at Advisian, a Worley Company. He has 35 yr of experience in industry and consulting with heavy industry, power, manufacturing, environment and resource efficiency. His expertise is in the management of technology development programs for water, wastewater and energy needs of heavy industry, with an emphasis on process optimization/integration and innovation. Mr. Hodgkinson holds a BS degree in physical chemistry from the University of New South Wales and an MEngSc degree in process integration from Monash University in Australia. He is a Fellow of the Institution of Chemical Engineers and a Chartered Engineer, UK Engineering Council.

22nd ANNUAL
INTERNATIONAL ABOVEGROUND STORAGE TANK CONFERENCE & TRADE SHOW
April 15-17, 2020 | Orlando, Florida

This conference is designed for engineers, managers or other individuals involved with operations, construction, environmental compliance, spill prevention and response or management activities associated with aboveground storage tanks.

FREE TRADE SHOW

30th NISTM ANNIVERSARY

SCHEDULE OF EVENTS:

FREE EPA SPCC & FRP SHORT COURSE
April 14, 2020

WELCOME RECEPTION
April 14, 2020

13TH ANNUAL GOLF TOURNAMENT
April 14, 2020

NETWORK MIXER
April 15, 2020

FREE TRADE SHOW ENTRY
April 15-16, 2020

AST CONFERENCE
April 15-17, 2020

FOR ADVERTISING, SPONSORSHIPS, AND SPEAKER OPPORTUNITIES, CALL 800.827.3515 OR 011.813.600.4024

NISTM
NATIONAL INSTITUTE FOR STORAGE TANK MANAGEMENT

To Register, Call or Visit the Website:
800.827.3515 | www.NISTM.org
International 011.813.600.4024

J. FAN and **S. ANANTHANARAYAN,** Advisian, a Worley Company, Houston, Texas; and **A. HODGKINSON,** Advisian, a Worley Company, Atlanta, Georgia

Demineralized water system design: Considerations for the petrochemical industry—Part 2

Demineralized water treatment systems play an important role in the petrochemical industry. The ability to consistently supply demineralized water that is subsequently used for steam generation is essential for all types of steam cracking processes. During the conceptual design of demineralized water treatment plants, special attention must be paid to raw water source identification and the associated quality and reliability of the demineralized water desired. Other considerations include the nature of demineralized water demand, condensate return rates and amount of storage. As mentioned in Part 1 of this article (published in the March issue of *Hydrocarbon Processing*), a typical design decision matrix should consider raw water source selection, the type of pretreatment for suspended solids removal and the quality desired by other users (utility and cooling water makeup). Part 2 discusses common technologies considered for water demineralization, along with some considerations for demineralized water treatment plant design optimization.

Ion exchange (IX) process. In the IX process, ions of a given species are displaced from an insoluble exchange material—usually an organic resin. IX resins consist of an organic or network structure with attached functional groups. The exchange capacity is determined by the number of functional groups per unit mass of resin. Once the exchange capacity of the resin is depleted, the resin will begin to cease exchanging dissolved ions and must be regenerated prior to reuse.

Four major classes of resins in water treatment exist: strong acid cation (SAC), weak acid cation (WAC), strong base anion (SBA) and weak base anion (WBA). The type of resin selected is based on source water chemistry and constituents that must be removed. SAC resins are the most common resins used for softening and demineralization applications. SAC resin removes the non-carbonate hardness, and WAC resin removes hardness associated with alkalinity. Hence, weak acid resins are more suitable for high alkalinity water and for when the hardness-to-alkalinity ratio in the feedwater is greater than 1. SBA resins are used for dealkalization, de-silicization and organic trap applications, while WBA resin removes only the anions of the strong mineral acids such as sulfate, chloride and nitrate. Carbonate/bicarbonate and silica ions will pass through a WBA resin.

Typically, the selectivity of SAC is best for calcium and magnesium, and SBA resin is ideal for sulfate and nitrate. On a cation resin, the most weakly held ion is sodium, and silica is often the most weakly held by anion resins. Therefore, sodium and silica are usually the first to break through on bed exhaustion, and monitoring these offers a good means of confirming demineralized water purity.

WBA has a higher working capacity than SBA and offers good resistance to organic fouling—such as from the polymer carryover downstream of a clarifier and from total organic carbon (TOC). However, these resins do not remove silica and bicarbonate. SBA offers the lowest silica leakage, so WBA is typically paired with an SBA.

Degasifiers are commonly used to reduce alkalinity in decationized water by stripping CO_2, using air. This removes the loading of carbonate to the anion resin and results in lowered operating cost by reducing the frequency and associated cost of regeneration. However, the additional capital cost for a degasifier must be justified with a payback analysis and will depend on the raw water quality.

Mixed-bed systems. With both cation and anion exchanges, due to the acid base equilibria driving the exchange processes, there is a limit to how perfectly the ions can be removed. Thus, to obtain very-high-purity water, a mixed-bed deionizer—in which SBA and SAC are intimately mixed and contained in a single pressure vessel—is used. The combination of SAC and SBA resins allows for very low silica and low sodium leakage. A gel resin combination is most commonly used to allow for physical separation during regeneration. The two resins are mixed by agitation with compressed air so the mixed bed can be considered as an almost infinite number of anion and cation exchangers in series. In general, a mixed-bed IX step (**FIG. 3**) can lower the conductivity to result in demineralized water with less than 0.1 μS/cm and with an ionic silica content of less than 10 μg/l.

Waste stream management. IX resins must be removed from service and regenerated when the maximum allowable effluent concentration is reached. Ideally, this removal from service will take place slightly before sodium or silica breakthrough. The higher the total dissolved solids (TDS) in the water, the more frequently the resins must be regenerated. During regeneration, regenerant agents contact active exchange sites on the cation and anion resins, and replace the adsorbed ions by H^+ or hydroxide (OH^-), respectively. The common regenerant agents for cation and anion resins are mineral acid and caustic soda, respectively. The mineral acid used is often sulfuric acid due to lower cost, although hydrochloric acid is often preferred for superior regeneration performance.

The two main regeneration processes are: co-flow regeneration and counter-flow regeneration. For co-flow regeneration, regenerant flow is in the same direction as feed flow, while regenerant flow is in the opposite direction to feed flow for reverse flow regeneration. Hence, for reverse flow regeneration, the most highly regenerated resin is located at the point where, during normal operation, the deionized water leaves the resin vessel, which, in turn, leads to a better contaminant removal performance. In addition, counter-flow regeneration is more efficient in the use of water as compared with co-flow regeneration, since fast rinse and backwash are combined into one stage. Due to higher purity in the treated water, higher water efficiency, low leakage and less required regenerant, a reverse flow arrangement with uniform-particle-size resin offers the best regeneration performance. Co-flow regeneration systems are a little simpler in terms of valving and piping complexity.

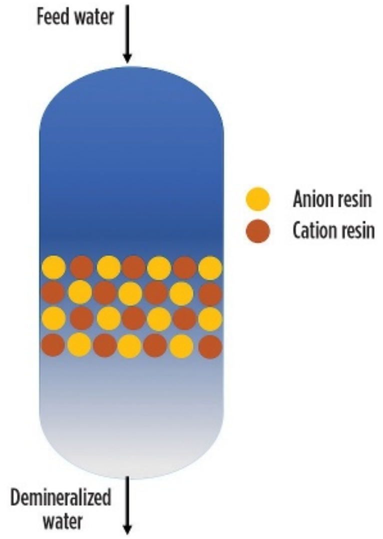


FIG. 3. Illustration of mixed-bed IX.

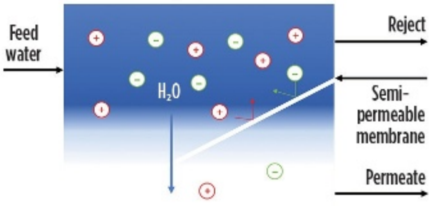


FIG. 4. Illustration of RO.

Regeneration can take place onsite or offsite. Onsite regeneration is typically utilized for large-volume users with more than 45 m^3/hr (20 gpm).[9] After onsite regeneration, the resin will be rinsed with treated water—a consumption that must be allowed for in system design. The regenerant waste must be treated before disposal. The common treatments for regenerant waste include pH neutralization and commingling with other waste streams for final disposal. For smaller systems [< 45 m^3/hr (20 gpm)], regeneration can be conducted offsite by a service contractor. The contractor will remove the exhausted IX exchange vessels and swap them out with pressure vessels containing regenerated resin. Offsite regeneration systems are much lower in capital cost than onsite regeneration due to the elimination of chemical handling equipment and storage facilities. However, offsite regeneration incurs higher operating costs and associated logistical issues that may hinder operational stability.

Advantages and limitations. Mixed-bed IX removes most impurities, except colloidal silica and nonionic organics. The system can be regenerated based on conductivity or silica concentration. However, mixed-bed systems normally have a lower resin capacity and a more complicated operating procedure because of the separation and remixing steps during the regeneration process. In addition, a separate acid or caustic regeneration system requires regenerant waste neutralization.

TABLE 4. Comparison of different RO membranes[10–12]

	PA	CA	PS
Sodium chloride (NaCl) rejection, %	> 98	90	95
Permeate flux	22 l/m^2/hr (lmh)–34 lmh or 13 gal/ft^2/d (gfd)–20 gfd	27 lmh–30 lmh or 16 gfd–18 gfd	75 lmh–94 lmh or 44 gfd–55 gfd
Chlorine tolerant	No	Yes	Yes
Cost	Medium	Low	High

Reverse osmosis (RO). RO is a membrane separation process capable of removing molecules with a molecular weight higher than approximately 200 daltons (Da), such as most colloids, naturally occurring organics, bacteria and pathogens from water (**FIG. 4**). RO is also able to remove both cations and anions. In the RO process, water is forced through a semi-permeable membrane at a pressure greater than the osmotic pressure characteristic of that water to produce a low-salinity permeate. The dissolved salts are retained on the reject side of the membrane, while water with minimal dissolved salts passes to the permeate side of the membrane. A continuous waste bleed stream, or reject, is maintained that sweeps salts from the membrane surface. This prevents the salt concentration from accumulating so much that the osmotic pressure exceeds the applied hydrostatic pressure, and permeation ceases.

Types of RO membranes include cellulose acetate (CA), polyamide (PA) and polysulfone (PS). **TABLE 4** compares the performance of these types. The most common choice for demineralization is PA. Pretreatments for RO include suspended solids removal, softening, ultrafiltration and disinfection to prevent scaling and biofouling.

The common configurations for RO systems are a one-pass RO or a two-pass RO. In a one-pass RO, the permeate has passed through an RO membrane just once. In a two-pass RO, the permeate from the first pass is treated a second time to produce a higher-quality permeate. With a two-pass RO, more than 99% of salt removal is usually achieved.

Waste stream management. RO recovery and reject stream flowrates vary by water source, and are primarily dictated by the solubility limits of sparingly soluble salts like calcium, strontium and barium salts. For a surface water system, a typical design for RO will have recoveries between 70% and 85%. Recovery from seawater will be lower at around 45%. Generally, reject quantities increase (i.e., recovery ratio decreases) with higher dissolved salt concentration in the water because the higher TDS tends to include more sparingly soluble salts. Higher salinity is not necessarily a cause of low recovery, but it will require higher operating pressures. The RO reject stream is often blended with other wastewater at the site for final disposal. Unless mandated by disposal requirements, it is uncommon to see the use of additional volume reduction processes, such as evaporation and/or crystallization on the reject stream, as these processes are typically very expensive to install and operate.

Advantages and limitations. A key advantage of RO systems, compared to IX processes, is that they have a relatively low chemical consumption and tend to have a more continuous operation—although they do require periodic shutdowns for cleaning. This is particularly advantageous when the influent TDS is higher than a few hundred mg/l. RO permeate can sometimes be suitable for boiler feedwater without further treatment, but it is often paired with a mixed-bed IX system for final permeate polishing. RO also removes colloids, including silica and a wide range of nonionic organics.

Even though RO produces high-purity water, the overall purity is usually not comparable with IX treatment unless the feedwater is already of good quality or a two-pass system is used. RO systems do not achieve as much removal of reactive silica as IX systems, but are much better at removing colloidal silica.

IX systems are a little more tolerant of poor pretreatment than RO, for which a robust pretreatment is essential to prevent membrane scaling and fouling. Several ions must be reduced before feedwater enters RO due to their scaling and fouling propensity. In general, the iron or manganese should be treated to less than 0.05 mg/l, barium to less than 0.01 mg/l, strontium to less than 0.01 mg/l, aluminum to a minimum, and silica to less than 20 mg/l.

In addition, RO operation is more sensitive to temperature. The rate of water permeation through the RO membrane increases as the feedwater temperature increases, since the viscosity of the solution is reduced and a higher diffusion rate of water through the membrane is obtained. Additionally, temperature more significantly impacts salt rejection performance in RO than in IX. Although the absolute operating range for RO is around 2°C–38°C, it has been reported that the optimum RO operation temperature is 25°C (77°F) and the upper temperature limit is around 35°C (95°F) to avoid membrane damage.[13] Conversely, IX can operate over a wider temperature range, including, if necessary, down to 0°C (32°F). Hence, preheating of the water may be required to achieve consistent RO performance when low water temperature is experienced.

Feedwater TDS concentration will also impact the RO performance, with higher feedwater TDS concentration decreasing permeate flow for the same feed pressure because the osmotic pressure increases, giving less net driving force to sustain permeation. A comparison of permeate flow under different TDS concentrations is shown in **FIG. 5.**

Another membrane-based technology called forward osmosis (FO) has attracted attention in both academic research and industrial development in the past 5 yr. Unlike RO, which uses pressure to drive flow through the membrane against the osmotic pressure gradient, FO utilizes a concentrated solution with a higher osmotic pressure than the feedwater to draw water from the feedwater into a "draw solution." The draw solution, diluted by the perme-

Jan Pawlewitz
Senior Vice President,
North America
Siemens

Johan Palm
Program Manager,
Digital Project Delivery
Hatch

Andrew Burt
BIM Systems Architect
Hatch

ON-DEMAND WEBCAST

The Digital Twins of Process Plants in Practice—Improving Resilience and Performance

Jointly developed for the process industry by Siemens and Bentley, PlantSight is an open, cloud-based solution that makes it possible to collect, connect, contextualize, validate and make use of all existing plant data. It creates a complete, reliable and updated digital twin of a plant, not only integrating 1D, 2D and 3D data, but also bringing visibility to dark data, which is a type of unstructured and unlinked data.

The speakers will cover a real user experience, showing how PlantSight made it possible to achieve a new level of collaboration across all disciplines and all levels. They will discuss how new cloud services are changing the way they work, and how this is enabling them to derive and deliver greater value from their assets and resources.

Listen for Free:
HydrocarbonProcessing.com/Webcasts

SIEMENS Ingenuity for life
Bentley® Advancing Infrastructure
HYDROCARBON PROCESSING®

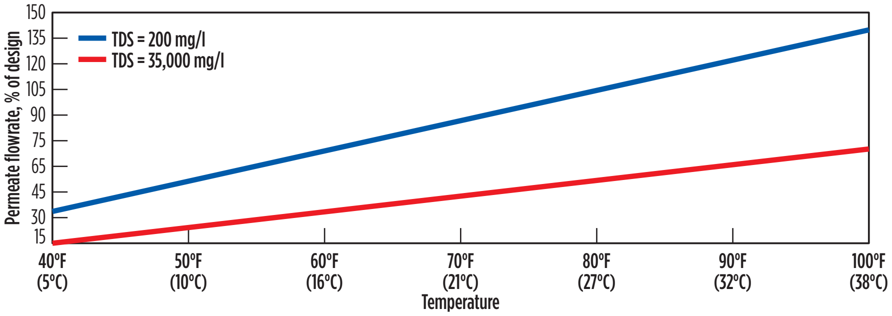


FIG. 5. Effect of temperature and TDS on permeate flowrate at constant pressure.

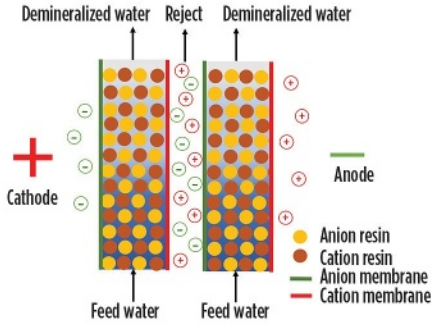


FIG. 6. Illustration of EDI.

ate drawn through the membrane from the feed stream, is reconcentrated to produce purified water and to recover the draw solutes. FO is reported to have several advantages over RO; however, the feasibility and reliability of FO systems on a large scale have not yet been widely demonstrated.

Electrodeionization (EDI). EDI utilizes electricity, IX membranes and resins to deionize water and separate dissolved ions from water. Each EDI module consists of five primary components: IX resin, two IX membranes (cation and anion exchange) and two electrodes (cathode and anode). When flow enters the EDI module, strong ions are scavenged out of the feed stream by mixed-bed resins. Under influence of a strong direct current field applied across the stack of components, charged ions are pulled off the resin and drawn toward the respective, oppositely charged electrodes. In this way, these charged strong-ion species are continuously removed and transferred into adjacent concentrating compartments (**FIG. 6**).

As strong ions are removed from the process stream, conductivity of the stream is reduced. The strong applied electrical potential splits water at the surface of the resin beads to produce hydrogen and hydroxyl ions. These act as continuous regenerating agents of the IX resin. Like IX, EDI can remove more than 99% of dissolved solids, except for colloidal silica.

Waste stream management. An EDI system typically converts 80%–95% of feedwater into product water, and the waste stream contains the same contaminants as in the feed, with 5–20 times higher concentration.

Advantages and limitations. The design of EDI provides continuous regeneration of IX resin without acid or caustic handling. EDI will also provide more consistent water quality in a compact space with low operating costs, provided power is available and its costs are acceptable.

However, EDI can be used only for water with hardness less than 1.5 mg/l to prevent calcium carbonate precipitation. Other drawbacks for EDI include a relatively high capital cost, high EDI stack replacement costs (a typical EDI stack lifetime is 5 yr) and difficulty in removing weakly ionized contaminants, such as silica, CO_2 and organics. Tanaka has compared the lifetime cost between EDI and IX and reported that, with an increase of TDS in the feedwater, EDI becomes increasingly cost-effective,[14] up to the previously mentioned water quality constraints.

However, detailed site-specific comparisons must be conducted. In addition, EDI is susceptible to fouling by colloidal silica or organic material typically found in the surface water, such as humic, fulvic or tannic acids.[15] Any ionic species formed from CO_2 gas will lower outlet resistivity of water produced by EDI, leading to decreased treatment efficiency. Hence, CO_2 management is required for an EDI system. At present, EDI systems are available only with plastic piping due to the danger of accelerated corrosion from stray currents.

For these reasons, EDI can be a good alternative to mixed-bed IX treatment, especially if paired with a two-pass RO, with which it can provide a demineralized water production system with low chemical consumption.

Electrodialysis reversal is another variation on EDI, where the polarity of the stack is reversed at a predetermined frequency. This technology is mostly suited for high-silica water (> 50 mg/l). It has lower capital cost, a larger footprint and higher operation and maintenance cost requirements when compared with RO, which is typically preferred when silica concentration is lower.

Thermal distillation (evaporation/condensation). The thermal distillation process requires thermal energy to form pure water vapor by heating the raw water source. This water vapor is then condensed on a cooling surface to collect as freshwater. Three thermal distillation technologies have emerged and are used commercially: multiple-stage flash (MSF) distillation, multiple-effect distillation (MED) and vapor compression (VC).

MED consists of several consecutive stages that are maintained at a decreasing level of pressure or temperature. In each stage, feedwater is heated by steam in tubes, causing evaporation of water. This newly generated steam flows into the tubes of the next stage (effect), heating and evaporating more water. Each stage essentially reuses energy from the previous stage, with successively lower temperatures and pressures after each one. Each stage mainly contains a multiphase heat exchanger.

In the MSF process, freshwater is produced in an evaporator of each stage by flashing some hot feed saline water due to low pressure. The produced water vapor passes through a demister to remove the entrained brine droplets and condenses on the external surface of the heat exchanger. The heat released from condensation is transferred to the flowing feed seawater through successive stages, resulting in increasing its temperature.

The VC distillation process is based on the principle of reducing boiling-point temperature by reducing the pressure over the liquid. Two methods are used to create the low pressure to evaporate incoming seawater: a mechanical vapor compressor (MVC), which is electrically driven; and a steam jet [thermal vapor compression (TVC)], which

TABLE 5. Demineralized water technology summary

	IX	RO	EDI	MED-TVC
Typical recovery,[1] %	95	70–80	80–95	30–40
TDS removal efficiency, %	> 99	90–99	> 99	> 99
Colloidal SiO_2 removal	No	Yes	No	Yes
Pretreatment complexity	High	High	High	Low
Operation temperature	< 85°C (< 185°F)	18°C–35°C (65°F–95°F)	10°C–38°C (50°F–100°F)	49°C–71°C (120°F–160°F)
Waste stream treatment	Yes	Yes	No	No (but might be subject to temperature restrictions)
Energy consumption, kWh/m^3	1–1.5	3.3–5[2]	0.7–3.7	1–1.4[2,3]
Total electrical energy equivalent,[19] kWh/m^3	1–1.5	3.3–5	0.7–3.7	11–28
CO_2 generation,[4] kg CO_2/m^3	1–2	2–6	0.7–4	25–30

[1] Fraction of feed converted to demineralized water

[2] Range shown for seawater; brackish water is approximately 0.5 kWh/m^3–1.5 kWh/m^3 for an RO system

[3] GOR of greater than 12

[4] CO_2 intensity of each process depends greatly on the CO_2 intensity of the inputs

is driven by low-temperature heat. The VC could be combined with MED designs to improve the energy efficiency of MED plants by taking advantage of exhaust steam from a steam turbine [usually 250 kPa–300 kPa (36 psi–43 psi)].[16] However, the higher the steam extraction pressure, the higher the electrical equivalent that is sacrificed to drive the desalination process.

The performance of distillation processes is measured by a dimensionless parameter known as gain output ratio (GOR), which is defined as the mass of distilled water per mass of input steam. Typically, higher GOR systems cost more, but consume less energy; therefore, they have lower operating costs. The GOR of MSF plants range from 8–12, 10–14 for MED, and 14–17 for TVC-MED.[17] Thermal distillation technologies are mostly used in regions where cheap energy is available, and they are often coupled with electricity production. The TDS in thermal distillation effluent is less than 5 mg/l.

Waste stream management. Like EDI, no additional chemicals are added into the thermal distillation process. Hence, the waste stream can often be discharged directly to an ocean outfall via a high-dilution diffuser.

Advantages and limitations. Due to high energy consumption and high capital cost, MSF is generally the process of choice for dual-purpose facilities (i.e., electric power and water production) and for applications that cannot be performed by other means, such as hypersaline groundwater. MSF has proved to be more economically favored than RO when energy costs are low, or when a waste heat source is available. MED combined with TVC has lowered capital cost and reduced power consumption. It has been reported that MED and MED-TVC require less electricity (1 kWh/m^3–1.4 kWh/m^3) as compared with RO (3.3 kWh/m^3–5 kWh/m^3), while MSF energy consumption is estimated around 4 kWh/m^3–6 kWh/m^3.[17] The lower energy consumption rate can make MED-TVC more economically comparable with RO, if there is no lost electrical generation.

In terms of pretreatment, the distillation process only requires simple pretreatment to avoid scaling and foaming by adding acid or advanced scale-inhibiting chemicals and anti-foaming reagents. In addition, the thermal distillation process is more tolerant to operational upsets and water quality variations.

However, the intensive combustion process for thermal distillation might pose environmental concerns associated with greenhouse gases. The CO_2 emissions for MED, MSF and RO are calculated to be 26.9 kg CO_2/m^3, 34.7 kg CO_2/m^3 and 4.3 kg CO_2/m^3, respectively.[18] Hence, for areas subject to a carbon tax or where CO_2 emissions are constrained, RO likely remains the more favorable process.

TABLE 5 summarizes the different demineralized water technologies.

Optimized design for demineralization. In general, relability and cost considerations must be evaluated during a demineralized water treatment plant design optimization. In this article, we have focused on design reliability, since it is an important consideration for the petrochemical industry, where demineralized water is a critical input to maintain operations. For demineralized water system design, both inherent reliability and mechanical reliability must be taken into consideration. Inherent reliability is the probability that the treatment plant can supply the demineralized water specification under all likely feed and demand conditions, while the mechanical reliabilty is related to the key pieces of equipment in the plant where failure may impact the demineralized water production rate.

Good data collection and a design appropriate to incorporate variabilities in demineralized water demand will improve the inherent reliability. For example, it is prudent to have a demand characterization workshop with all the demineralized water users. This allows for demand development to consider abnormal conditions such as plant outages; condensate dump (due to contamination); rate of condensate return during freezes; startups; and plans for more frequent occurrences, such as furnace decoking. Based on the workshop for demineralized water, demand rate curves can be developed. The demand curve can then be utilized to develop the design flowrate for the demineralized plant.

To achieve better mechanical reliability, a flexible equipment arrangement might be considered. Common configurations for demineralized water treatment include 2 × 100%, 2 × 75% and 3 × 50%; other configurations, such as 7 × 20%, have also been used. In general, a demineralized system should be adequate to accommodate sudden variations in water demand and allow isolation of an entire treatment train without impacting production, for maintenance flexibility. For example, in a 3 × 50% configuration, all major unit processes have three identical units, such that any two units operating at 100% capacity can meet the overall water demand.

Temporary and mobile water treatment systems also might be considered to handle short-term demineralized water demand. For example, using a third-party provider that supplies demineralized water treatment equipment in a mobile or a semi-permanent trailer format is an approach that many sites are considering for managing demand shortfalls during sustained peak events. It may make sense during the project planning stages to include a site footprint for trailers and tie-ins as part of a larger strategy to optimize the demineralized plant capacity. Some buffer treatment capacity can be built into the pretreatment processes (clarification and filtration) to allow for feeding of the third-party trailers during campaign events.

Providing adequate storage of demineralized water is another item that should be considered as part of the plant design discussion. Storing 12 hr–24 hr (or more, depending on site-specific needs) of demineralized supply, along with sufficient redundancy in the design, can allow for a guaranteed shutdown period, over which maintenance or retrofits can be made. This storage can also be used as a buffer capacity to fulfill instantaneous peak demand without incurring significant operating costs. The right amount of storage usually boils down to economics, available footprint and criticality of operations supported by the demineralized plant, and this is usually derived by reliability modeling.

Demineralized water system reliability analysis must consider critical factors such as the impact of water quality variations (both temperature and chemistry) on the type of demineralized technology selected, along with fluctuations in demineralized water demand and plant redundancy. In addition, if a demineralized treatment system is coupled with other facilities within the chemical complex—such as waste heat generated from cogeneration or a power plant—by using exhaust steam to preheat feedwater or to drive thermal desalination, then additional reliability analysis must be conducted to eliminate potential single points of failure.

In the authors' experience, an optimum configuration for demineralized water treatment employs both RO and IX processes. IX is typically preferred where there is a constraint on the volume of wastewater generated, where feedwater temperature is less than 18°C (65°F) year-round, where power costs are high (> $0.10/kWh), or where feedwater TDS is substantially less than 500 mg/l. At temperatures below 18°C (65°F), it is unlikely that RO without feedwater preheating (which typically is cost-prohibitive if there is no waste heat available) will be economical. RO tends to be more economical as feed salinity increases. Variations in water quality resulting from prolonged drought might result in an increase of TDS by 20%–30% in some watersheds. RO tends to be more suitable for handling these swings in TDS, provided there is adequate reserve capacity. Other site-specific factors—such as available footprint, expandability of the plant, operability, and availability of skilled water treatment operators—must be considered in the selection of a demineralized technology.

In many cases, a combination of RO with IX resins (in mixed-bed configuration) provides a robust water quality and offers the potential for lower lifecycle costs than either IX or RO alone. This is primarily driven by decreased TDS loading on IX resins and reduced chemical demand due to performing the main work of TDS removal using RO. RO typically reduces TDS to less than a few tens of mg/l, resulting in a higher IX resin efficiency. Decreased TDS loading on an IX system decreases the frequency of regeneration and reduces waste, leading to lower overall operational cost of demineralized water.

Takeaways. Demineralized water treatment design is critical to ensure high-purity steam generation. Proper pretreatment for suspended solids removal must be evaluated based on various raw water sources. No one formula exists for choosing a demineralization technology. As demonstrated throughout this article, a wide range of factors should be considered, and data should be gathered and assessed on a case-by-case basis. A methodical consideration of the issues outlined in this article will lead to a demineralized plant design that reliably supports refinery operation.

LITERATURE CITED

[9] Kanegsberg, B. and E. Kanegsberg, *Handbook for Critical Cleaning: Cleaning Agents and Systems,* CRC Press, 2011.

[10] Christophersen, D., *Understanding differences of boiler feedwater pretreatment equipment,* Veolia Water, http://www.veoliawatertech.com/crownsolutions/ressources/documents/2/21881,Water-pp53-84.pdf

[11] Allegrezza, Jr., A., et al., "Chlorine resistant polysulfone reverse osmosis modules," *Desalination,* 1987.

[12] Riley, R., H. Ridgway and K. Ishida, "Polyamide reverse osmosis membrane fouling and its prevention: Oxidation-resistant membrane development, membrane surface smoothing and enhanced membrane hydrophilicity," Separation Systems Technology Inc., San Diego, California; Orange County Water District, Fountain Valley, California, 2000.

[13] McGovern, R. K., "On the potential of forward osmosis to energetically outperform reverse osmosis desalination," *Journal of Membrane Science,* 2014.

[14] Tanaka, Y., "Ion exchange membranes: Fundamentals and applications, Series 12," *Membrane Science and Technology,* Elsevier, Netherlands, 2007.

[15] Smith, B. and B. Hyde, *Short-bed demineralization: An alternative to electrodeionization,* 6th International Conference on Cycle Chemistry in Fossil Plants, Columbus, Ohio, June 2000.

[16] Wei, J., *Utilization of exhaust steam of waste to energy (WTE) power plants for water desalination,* Columbia University, 2017, online: http://www.seas.columbia.edu/earth/wtert/newwtert/Research/sofos/Wei_thesis_Oct2017.pdf

Complete literature cited available online at HydrocarbonProcessing.com.

JINGJING FAN is a Wastewater Process Engineer at Advisian, a Worley Company. She has experience in water and wastewater treatment design for the petrochemical and refining industries. Dr. Fan holds a PhD in environmental engineering from the University of Houston.

SRIRAM ANANTHANARAYAN is a Lead Process Engineer/Project Manager with Advisian, a Worley Company. Mr. Ananthanarayan has more than 15 yr of experience in the process design, engineering and evaluation of water and wastewater treatment systems. He has led and developed designs to support projects in the oil and gas, chemicals, power and mining industries. He earned a BS degree in chemical engineering from the University of Calicut and an MS degree in civil engineering from Colorado State University.

ANDREW HODGKINSON is the Global Technical Leader at Advisian, a Worley Company. He has 35 yr of experience in industry and consulting with heavy industry, power, manufacturing, environment and resource efficiency. His expertise is in the management of technology development programs for water, wastewater and energy needs of heavy industry, with an emphasis on process optimization/integration and innovation. Mr. Hodgkinson holds a BS degree in physical chemistry from the University of New South Wales and an MEngSc degree in process integration from Monash University in Australia. He is a Fellow of the Institution of Chemical Engineers and a Chartered Engineer of the UK Engineering Council.